Quasicrystals / Quasicristaux

A celebration of the pioneering work on quasicrystals in France and the expansion of crystallography ☆

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Des travaux pionniers sur les quasicristaux en France et l'expansion de la cristallographie

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ABSTRACT

The coincidence of a meeting at CECM/CNRS in 1985 to plan work on the newly discovered quasicrystals with a meeting at IHES on hyperspace crystallography greatly expanded crystallography and made France a major player in the opportunities provided by this discovery. Adherence to a paradigm which forbade possible symmetries for sharply diffracting solids discouraged US crystallographers from the field. Even though there were many earlier warnings and amendments to this false paradigm, it was considered by many to be a defining law of crystallography. By 1992, the International Union of Crystallography changed the definition of crystals to include quasicrystals. This definition still excludes many ordered structures, like a recently studied isotropic metallic structure that is as strongly ordered as a related intermetallic crystal.

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RÉSUMÉ

La simultanéité d'une réunion au CECM/CNRS en 1985 planifiant le travail expérimental sur les quasicristaux nouvellement découverts et un atelier mathématique à l'IHES sur la cristallographie *N*-dimensionnelle a permis un développement des concepts de la cristallographie moderne et fait de la France l'un des acteurs majeurs du domaine. Concomitamment, aux États-Unis, les cristallographes se dissuadèrent d'aborder ce sujet du fait du paradigme interdisant certaines symétries aux solides présentant des diffractions ponctuées, qui était tenu par un grand nombre pour la loi fondamentale de la cristallographie, malgré de nombreux exemples et exceptions (non-stœchiométrie, phases incommensurables, etc.). En 1992, l'Union internationale de cristallographie changea la définition du cristal pour y inclure les quasicristaux. Cette définition exclut toujours de nombreuses structures ordonnées, telle une structure métallique isotrope récemment découverte, qui est aussi ordonnée que le cristal intermétallique dont elle dérive.

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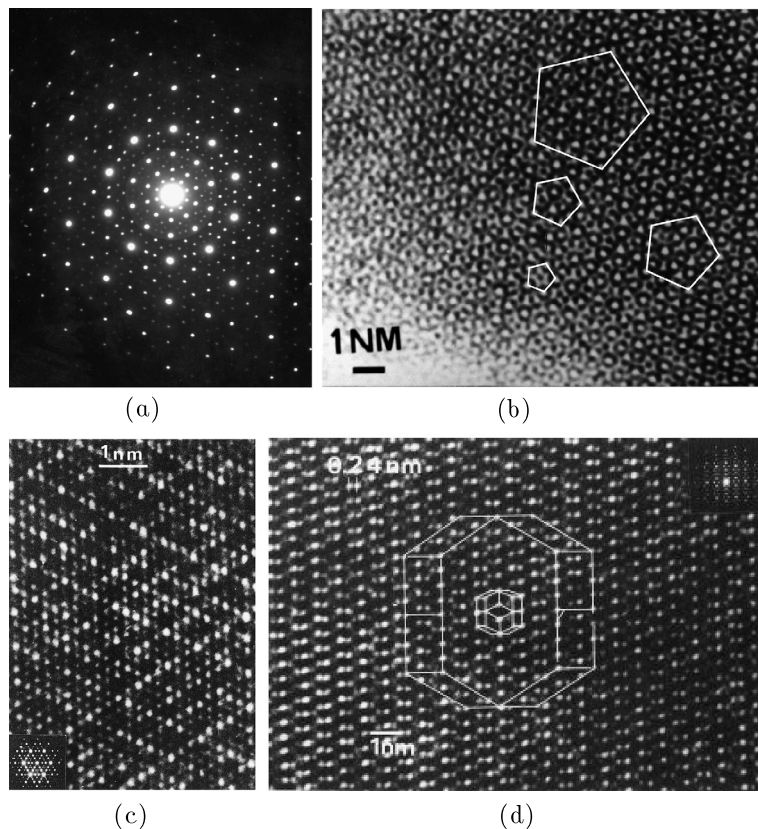Open access under CC BY-NC-ND license.

(a) (b)

(c) (d)

Fig. 1. Original early 1985 high resolution images of the Al–Mn quasicrystal provided by Richard Portier [4] showing the Fibonacci sequences of interplanar spacings. The diffraction pattern (a) and image (b) from the 5-fold axis and the images from the 3-fold (c) and 2-fold (d) axes.

1. The early contributions

Dan Shechtman discovered the Al–Mn quasicrystals with electron diffraction and dark field imaging in the spring of 1982 during his sabbatical at NBS. Shechtman showed me only the five-fold diffraction pattern which I dismissed as twinning. No one else seems to have been convinced by what they were shown. Nothing more was done for two years. Shechtman continued to work at NBS on other tasks until he returned to teach in Israel for the academic year 1983–1984. In the spring of 1984 Ilan Blech at the Technion became interested and created an icosahedral glass model that gave a similar diffraction pattern. This encouraged Shechtman to submit a paper with Blech to the Journal of Applied Physics that was rejected[1] as boring metallurgy. Because Blech was about to leave academia to return to a brilliant career in Silicon Valley, this model is his only contribution to quasicrystallography.

When Shechtman returned to NBS, which had become NIST, in August 1984 he showed me the rejected manuscript, and I realized that the experiments made a compelling case that needed to be sent to the Physical Review Letters. He asked me to join him in preparing a new manuscript. On a visit to Santa Barbara a month later, I gave an extemporaneous talk about what had been discovered. It was fortunate for the field — and the French involvement that was celebrated by the French Academy in 2012 — that Denis Gratias was in that audience. He returned with me to meet Shechtman, to subject the material to his own tests, and to participate in the writing of the paper [2]. From the outset, Gratias had many ideas about what needed to be done. Our paper was submitted on October 7th and in print three weeks later. There were immediate positive responses. Levine and Steinhardt [3] had seen our draft and were in print by December 1984. Already the March 1985 meeting of the American Physical Society had a session on quasicrystals with 13 contributed papers.

In January 1985, Gratias invited Shechtman and me to CECM–CNRS (Vitry, France) to plan our work together with Richard Portier who had already provided high resolution electron microscopy pictures as those seen in Fig. 1 showing the Fibonacci sequences in the interplanar spacings [4] and self-similar geometric features with the golden mean τ and τ^3 as scaling units. By a happy coincidence there was a workshop at the Institut des Hautes Etudes Scientifiques (IHES) on higher dimensional crystallography organized by Louis Michel and Marjorie Senechal [5]. Within days André Katz and Michel Duneau provided a most important talk [6] at this IHES workshop. The first international conference on quasicrystals was planned in Les

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[1] This paper was revised and sent to Metall. Trans. [1].

Houches [7] organized by Louis Michel and Denis Gratias. So began the amazingly fruitful and dominant French involvement in quasicrystals. It is indeed a great pleasure for me to participate in the celebration of the rich and profound contributions of French scientists to the field of quasicrystals.

From the beginning there were many confirmations of the existence of quasicrystals. Beyond the decagonal phase discovered at NIST by Bendersky [8] other icosahedral quasicrystals, some stable, were found [9]. Examples of two space groups, $Pm\bar{3}5$ and $Fm\bar{3}5$, and an ordering transition between them were studied. Quasicrystals with 5-, 8-, 10- and 12-fold axial symmetries were found.

It was a revolution in crystallography which was enlarged, but with strong opposition to overthrowing the *fundamental law* as will be discussed next. Linus Pauling was the most vocal opponent and his papers [10] influenced American crystallographers from contributing.

2. What law was endangered and why the opposition?

Two centuries ago, René Just Haüy [11] hypothesized that the shapes of some crystals could be rationalized by assuming that these crystals where composed of identical molecular units arrayed periodically on a three dimensional lattice. Haüy could not imply that all crystals would be this way, but it became the starting point for the development of a sophisticated mathematical and scientific crystallography in the 18–19th centuries.

Catalogs were created of all possible symmetries for these crystals: 7 crystal systems, 11 Laue groups, 14 lattices, 32 crystallographic point groups, 51 crystal forms, 230 space groups, etc. No other symmetries would be possible for such crystals. Discrete diffraction, based on this idea, became the important tool of 20th century crystallography. Because no exceptions were found in almost 200 years, it became accepted that all crystals were regular arrays on a lattice, and became a law or a paradigm that arose from experience, rather than from fundamental principles.

The icosahedral Al–Mn solid was an exception. It could have been accepted as another non-crystalline solid. But its sharp diffraction peaks implied crystallinity, and therefore violated the paradigm. The finding was challenged. The solid was proposed as composed of a classical crystal with a very large unit cell, complex modulations, or a five-fold twin, or in combinations. None of the suggestions survived experimental and/or theoretical scrutiny.

That Haüy's hypothesis became a law applicable to all crystals is surprising for other reasons. During the 200 years the hypothesis of periodically arrayed identical unit cells survived many amendments necessitated by many experimental findings: Haüy's crystals had to be *stoichiometric compounds*, obeying the law of definite proportions based on the rational content of any of the identical unit cells. Non-stoichiometry was an anomaly, not compatible with periodicity. It took a century to sort out its various causes; defects, solids that absorbed fluids, and mixed crystals were among the many ideas proposed. Solid solutions, *i.e.* solids with indefinite proportions, were especially difficult. For crystallography, it was very important for all these cases that the limits on crystal symmetries remained when Haüy's hypothesis was amended to permit defects and allow unit cells to have different mixes of species.

Although irrationally modulated structures have been known for a century, these quasiperiodic structures did not cause a revolution because they also conformed to the symmetry limitations, if the modulations are ignored. Research on these structures was important for our work on quasicrystals, because they could be modeled with *higher dimensional crystallography* [12]. Magnetic crystals with irrationally spiral spins is another case that conforms to the symmetry limitations if the spins are ignored [13].

Modifications of paradigms to keep them successful are common. If a scientific revolution occurs they often were warning signs. The discovery of a sharply diffracting solid with the non-crystallographic icosahedral symmetry challenged only the universality of this paradigm. It took considerable time to be accepted by some crystallographers. Sharp diffraction implies quasiperiodicity; hence the name *quasiperiodic* crystals, shortened to *quasicrystals* [3].

Some paradigms survive a scientific revolution. Mechanics was greatly enlarged with quantum and relativistic effects, but Newtonian mechanics survives with well-known bounds on the ranges of validity. Other paradigms, like the ether in the 19th century, disappear entirely. Crystallography was enlarged by quasicrystals. Classical crystallography was not overturned. It continues to be applicable to crystals with lattices, and many of its techniques and concepts have found enlarged applicability. That this was a preserving revolution was understood from the beginning of quasicrystals. The intense short-lived opposition was a surprise.

Since 1991 the International Union of Crystallography has defined crystals as objects that exhibit sharp diffraction peaks [14]. Quasicrystals are now crystals by definition. Any of the 3-D point groups of finite order are now possible symmetries for crystals; an infinite set of point groups has been added to the 32, although only icosahedral and 5-, 8-, 10- and 12-fold axes have been observed.

3. What next? *The aperiodic zoo …*

Structural units repeat in both periodic and quasiperiodic solids. Both periodicity and quasiperiodicity allow the frequent repetition of low energy configurations. But any low energy motif that cannot fill space has to pair with some other higher energy configurations to create a crystal. For example low energy tetrahedra cannot fill space, but paired with octahedra they form close packed periodic crystals. We now know that quasiperiodicity provides the alternative packing of repeating configurations. When more chemical species are added to a solid, the likelihood of finding quasiperiodicity seems to
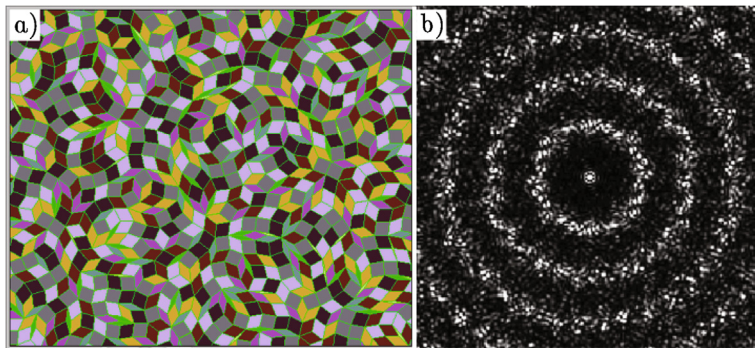
Fig. 2. (a) This tiling with 19-fold symmetry is quasiperiodic and long range ordered approximate a 2-D isotropic glass as shown on the corresponding diffraction pattern (b) created using the website of Steffen Weber, JCrystal (see http://jcrystal.com/steffenweber/JAVA/jtiling/jtiling.html).
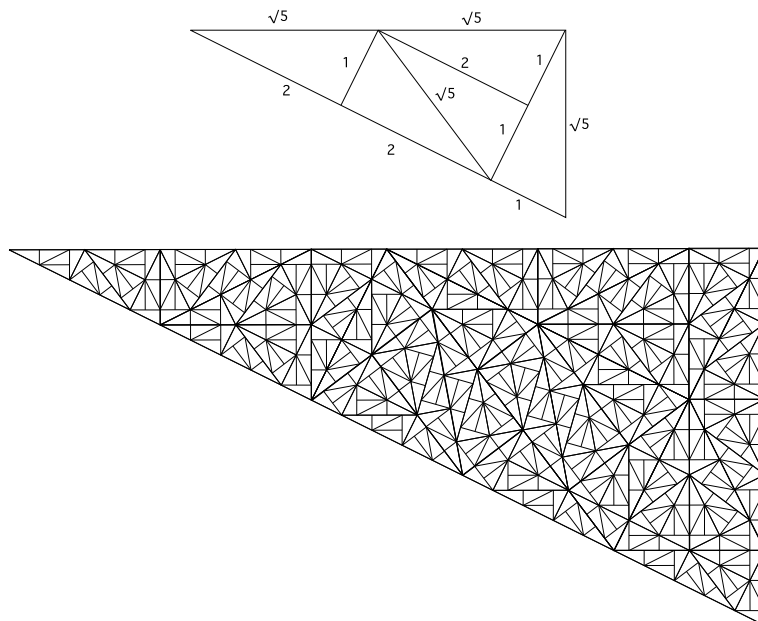

Fig. 3. At each decomposition step, every triangle in this Conway pinwheel tiling is subdivided into five congruent triangles with new orientations.

increase. But there are many other ordered arrangements that are neither periodic nor quasiperiodic that might be well suited for packing low energy configurations.

Should they be excluded objects treated by the techniques of crystallography?

In her book *Quasicrystals and Geometry*, Marjorie Senechal [15] devotes a chapter to *The aperiodic zoo*. This chapter is devoted to some of the many other ordered arrangements of points that are neither periodic nor quasiperiodic, and cannot be crystals by the current definition. Among this excluded set are a number of structures that can be studied by crystallographic methods. A recent study of an isotropic structure may be an example [16].

As a first geometric example in 2-D, consider tilings with *n*-fold symmetry as *n* increases. Fig. 2 shows a 19-fold tiling and its diffraction pattern. While this tiling with a finite value of *n* is quasiperiodic and ordered, it approximates an isotropic structure. Although its diffraction pattern is composed of dense discrete peaks, the intense diffraction peaks are clustered into broad rings reminiscent of a glassy structure. As *n* approaches infinity this structure becomes isotropic and no longer has discrete diffraction peaks. In this limit, the tiling ceases to be a 2-D crystal and could be defined as a 2-D glass. Does it make sense in this mathematical progression from tilings to glass to exclude the glass?

For another example, consider Conway's pinwheel tiling, as described by Radin [17], and shown in Fig. 3 after various decomposition steps. They are examples of ordered 2-D arrangements of points that are neither periodic nor quasiperiodic. They also are structures of identical triangular tiles, packed in an ordered way. In the figure there are a finite set of discrete line directions; earlier directions are longer than one the ones that arise later in the decomposition steps. In the limit of infinite decomposition steps all orientations appear, but the structure is not isotropic. Can there be a 2-D physical realization of adsorbate motifs in which the chemistry dictates triangular unit cells arranged in this way?

When crystallography was confined to lattices, unit cells had to be parallelepipeds. The 3-D Schmitt–Conway–Danzer tile is not a parallelepiped. It tiles 3-D space only in an aperiodic way, forming a spiral structure of periodically ordered layers with successive layers rotated from each other by an irrational fraction of π. Spiral structures are known to exist. With other tiles or combination of tiles, many other types of aperiodic tilings should be possible. Are there chemical or magnetochemical motifs that form such unit cells?

Computer simulations have identified a number of ordered non-crystalline structures. In 1992, Dzugutov [18] proposed an artificial potential for a single component system in which non-crystalline structures would have lower energies than crystalline structures. Simulations found a first-order reversible phase transition between a melt and a non-crystalline isotropic solid that is highly structured and has low entropy. One structure seems to be composed of long curved bodies whose cross-section has pentagonal symmetry. Mendelev [19] found a similar first-order reversible transition in a molecular dynamics simulation that used an early embedded atom potential for Al. He found an equilibrium melting temperature where the melt and the non-crystalline solid coexist along an interface. When the temperature is raised melting of the solid occurs only heterogeneously by motion of the interface, and not by homogeneous liquation throughout the solid. Below the melting temperature, the solid expands as the interface moves into the melt. Mendelev reported a latent heat and a volume change and a 10^4 change in diffusivity.

Occasionally failures create opportunities. In 1987 my colleagues were unsuccessful in creating a quasicrystal from a rapidly cooled Al–Si–Fe melt [20]. A primary solid formed from the melt. Because it rejected Al into the melt, this solid formed by a first-order transition. This solid grew from the melt like a crystal, but it proved to be isotropic. This unexpected result was noted [21,22], but not pursued. Recently we created from melts of different concentrations samples that were near 100% of three related phases: 1. this isotropic phase, 2. the icosahedral quasicrystal and 3. the crystalline α-AlSiFe. Using synchrotron radiation with a wavelength of 0.015359 nm, we were able to do high resolution diffraction and create radial distribution functions for all three phases. The isotropic phase showed strong ordering to 1.2 nm that was a closer to that in crystalline α-AlSiFe than to that in the quasicrystal. We demonstrated that this ordered isotropic solid phase is a solution phase with solidity limits with respect to melts at high temperature and against solids at lower temperatures [23]. Thus an ordered isotropic solid phase can occur in real systems. Whether it belongs to the zoo or is similar to what was seen in simulations remains to be seen. The enlargement of crystallography was a revolution. Can there be a further enlargement?

Acknowledgements

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